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(21) International Application Number: PCT/CA96/00370 (22) International Filing Date: 5 June 1996 (05.06.96) (30) Priority Data: 08/480,098 6 June 1995 (06.06.95) US (60) Parent Application or Grant (63) Related by Continuation US 08/480,098 (CIP) Filed on 6 June 1995 (06.06.95) (71) Applicant (for all designated States except US): BALLARD POWER SYSTEMS INC. [CA/CA]; 9000 Glenlyon Parkway, Burnaby, British Columbia V5J 5J9 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): STONE, Charles [CA/CA]; 411 - 237 East 4th Avenue, Vancouver, British Columbia V5T 1G6 (CA). STECK, Alfred, E. [CA/CA]; 3956 Westridge Avenue, West Vancouver, British Columbia V7V 3H7 (CA). LOUSENBERG, Robert, D. [CA/CA]; 209 - 235 West 4th Street, North Vancouver, British Columbia V7M 1H8 (CA).	(74) Agent: RUSSELL REYNEKE; Two Bentall Centre, Suite 700, 555 Burrard Street, Vancouver, British Columbia V7X 1M8 (CA). (81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	
(54) Title: SUBSTITUTED TRIFLUOROSTYRENE COMPOSITIONS (57) Abstract Sulfonyl fluoride substituted α,β -trifluorostyrene monomers are disclosed. The monomers are incorporated into polymeric compositions which are conveniently hydrolyzed to produce polymeric compositions which include ion-exchange moieties. The resulting compositions which include ion-exchange moieties are particularly suitable for use as solid polymer electrolytes in electrochemical applications, such as, for example, electrochemical fuel cells.		

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SUBSTITUTED TRIFLUOROSTYRENE COMPOSITIONS**Cross-Reference To Related Application**

This application is a continuation-in-part of U.S. Patent Application Serial No. 08/124,924 filed September 21, 1993, now U.S. Patent No. 5,422,411
5 issued June 6, 1995, entitled "Trifluorostyrene And Substituted Trifluorostyrene Copolymeric Compositions and Ion-exchange Membranes Formed Therefrom". The related application, incorporated herein by reference in its entirety, describes
10 polymeric compositions derived from copolymers of α,β,β -trifluorostyrene with a variety of substituted α,β,β -trifluorostyrenes. These compositions are suitable for use as, for example, membranes, particularly as ion-exchange membranes.

Field Of The Invention

The present invention relates to polymeric compositions derived from copolymers of α,β,β -trifluorostyrene with a variety of substituted α,β,β -trifluorostyrenes. More particularly, the present
20 invention relates to copolymers of α,β,β -trifluorostyrene and substituted α,β,β -trifluorostyrenes including sulfonyl fluoride substituted α,β,β -trifluorostyrene monomers. These copolymers are conveniently hydrolyzed to give polymeric
25 compositions with ion-exchange moieties. The resulting polymeric compositions which include ion-exchange moieties are particularly suitable for use as solid polymer electrolytes in electrochemical applications, such as, for example, electrochemical
30 fuel cells.

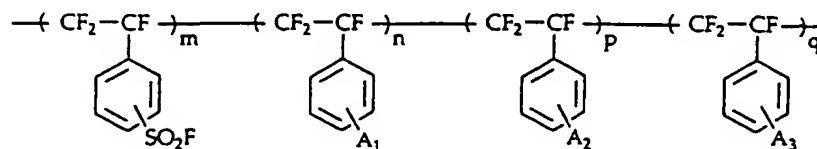
Background Of The Invention

Polymeric compositions, derived from copolymers of α,β,β -trifluorostyrene with a variety of substituted α,β,β -trifluorostyrenes, in which at least one of the substituents is an ion-exchange moiety have utility as ion-exchange membranes, as disclosed in related U.S. Patent No. 5,422,411 issued June 6, 1995.

Typically, ion-exchange moieties are introduced into copolymers containing unsubstituted α,β,β -trifluorostyrene units (so called "base copolymers") via aromatic substitution of at least a portion of those units. This typically involves preparation and purification of the base copolymer, followed by aromatic substitution and subsequent isolation and purification of copolymer containing the ion-exchange moiety. In an alternative approach for introducing ion-exchange functionality, an ion-exchange moiety or masked ion-exchange moiety is present in one or more of the monomers prior to copolymerization. The use of a masked ion-exchange moiety, which can be converted to the corresponding ion-exchange moiety via a simple procedure, can be advantageous.

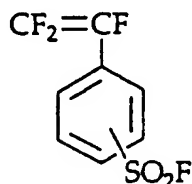
Summary Of The Invention

Polymeric compositions of the present invention include:



where m is an integer greater than zero, and n, p and q are zero or an integer greater than zero; A₁, A₂ and A₃ are selected from the group consisting of hydrogen, halogens, alkyls, perfluoroalkyls, CF=CF₂, CN, NO₂, OH, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

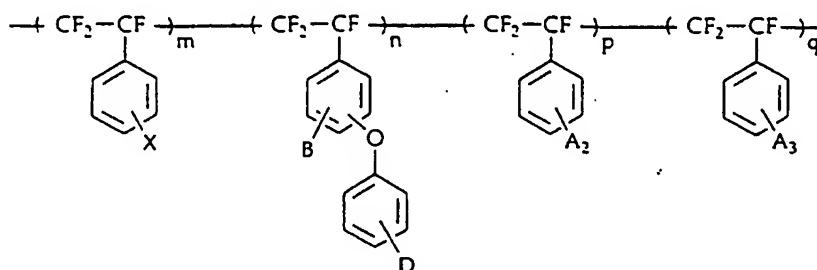
The above polymeric compositions are prepared by polymerization (where only m is an integer greater than zero) or copolymerization (where m is an integer greater than zero and at least one of n, p and q is an integer greater than zero) of monomer isomers having the chemical formula:



The sulfonyl fluoride moiety (-SO₂F) can be converted to a sulfonic acid (-SO₃H) moiety by conventional techniques such as, for example, hydrolysis. The A₁, A₂ and A₃ substituents may be further elaborated by known techniques such as, for example, hydrolysis of the CN group to form COOH or by reduction with common reducing agents (such as, for example, Raney nickel) to form a primary amine, thereby transforming the A₁, A₂ and A₃ substituents into ion-exchange moieties. Thus, the group from which A₁, A₂ and A₃ are selected may further consist of SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, OPO₃H₂, NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group

consisting of alkyls, perfluoroalkyls and aryls), and the resulting polymeric compositions may thus comprise the sulfonyl fluoride moiety and one or more type of ion-exchange moiety, and may also
5 comprise both cation-exchange and anion-exchange moieties.

Polymeric compositions of the present invention further include:



10 where n is an integer greater than zero, and m, p
and q are zero or an integer greater than zero; A₂
and A₃ are selected from the group consisting of
hydrogen, halogens, alkyls, perfluoroalkyls,
CF=CF₂, CN, NO₂, OH, O-R (where R is selected from
15 the group consisting of alkyls, perfluoroalkyls and
aryls); X, B and D are selected from the group
consisting of SO₂F, SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂,
COOH, OSO₃H, OPO₂H₂, OPO₃H₂, NR₃⁺ (where R is
selected from the group consisting of alkyls,
20 perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is
selected from the group consisting of alkyls,
perfluoroalkyls and aryls); and the group from
which D is selected further consists of hydrogen,
and when m is also an integer greater than zero and
25 X is SO₂F, the group from which B is selected
further consists of hydrogen. The group from which
A₂ and A₃ are selected may further consist of SO₃H,
PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, OPO₃H₂,

NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls). The resulting
5 polymeric compositions may thus comprise homopolymers and copolymeric compositions, and may also comprise polymeric compositions in which there is more than one ion-exchange moiety attached to a monomer fragment.

10 The substituents on the aromatic rings (SO₂F, A₁, A₂, A₃, X, B and D) may each be located in the ortho, meta or para positions, as indicated in the formulas wherein the chemical bond drawn for these substituents intersects the aromatic ring.

15 Copolymeric compositions of the present invention may be binary, ternary or quaternary.

The polymeric compositions of the present invention can also consist essentially of the above chemical units. Thus, the polymers could include
20 amounts of other monomers such as, for example, styrene.

Cross-linking is preferably introduced into the polymeric compositions of the present invention for applications in which it is, for example,
25 desirable to increase dimensional stability, reduce swelling, modify the mechanical properties, or control ion-exchange selectivity.

In accordance with convention in the art, the above chemical formulas for polymeric compositions containing more than two monomers (where at least
30 three of m, n, p, q are greater than zero) are intended to indicate that the monomers are present in the polymeric composition, but are not limited to the particular order in which the monomers are

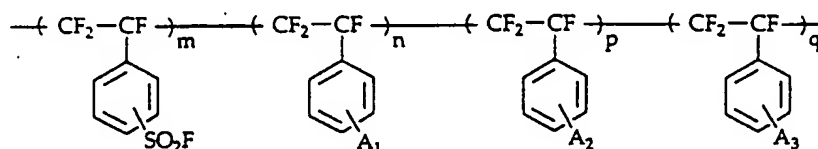
set forth in each general formula. For example, random linear copolymers and/or linear block copolymers formed from the indicated monomers are both contemplated.

- 5 The polymeric compositions of the present invention are suitably formed into membranes, and are preferably employed as ion-exchange membranes, most preferably as cation exchange membranes in electrochemical fuel cells.

10 Detailed Description Of The Preferred Embodiments

The polymeric compositions of the present invention are derived from copolymers of α,β,β -trifluorostyrene with a variety of substituted α,β,β -trifluorostyrenes.

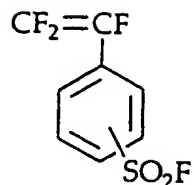
- 15 In one aspect, a polymeric composition of the present invention includes:



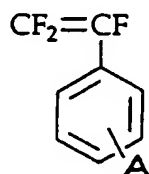
- 20 where m is an integer greater than zero, and n, p and q are zero or an integer greater than zero; A_1 , A_2 and A_3 are selected from the group consisting of hydrogen, halogens, alkyls, perfluoroalkyls, $\text{CF}=\text{CF}_2$, CN, NO_2 , OH, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

- 25 The polymeric compositions are produced by polymerization of a monomer having the chemical formula:

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In the embodiment where only m is an integer greater than zero, the resulting polymeric composition is homopolymeric. In the embodiment where m is an integer greater than zero and at least one of n, p and q is an integer greater than zero, the resulting polymeric composition is copolymeric. For copolymeric compositions, the above sulfonyl fluoride- α,β,β -trifluorostyrene monomer is reacted with other monomers selected from the group of substituted α,β,β -trifluorostyrenes having the chemical formula:



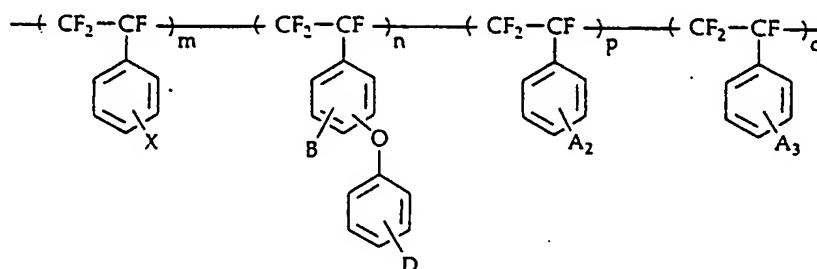
where A is selected from the group consisting of hydrogen, halogens, alkyls, perfluoroalkyls, $\text{CF}=\text{CF}_2$, CN , NO_2 , OH , O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

In a preferred method, the above monomers are mixed in an aqueous medium containing a free radical initiator and an emulsifying agent, at temperatures in the range of about 35°C - 100°C , and preferably in the range of 45°C - 65°C , for a time period of about 24 to 74 hours under an inert atmosphere. In general, the polymerization

procedures and techniques employed in the preparation of polymeric compositions of the present invention are known. A suitable reference for polymerization techniques is Textbook Of Polymer Science, 3rd Edition, by F.W. Billmeyer, Jr., published by John Wiley & Sons.

In a further embodiment of a polymeric composition of the above formula, m is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; the group from which A₁, A₂ and A₃ are selected further consists of SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, OPO₃H₂, NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls). The resulting polymeric compositions may thus comprise the sulfonyl fluoride moiety and one or more type of ion-exchange moiety, and may also comprise both cation-exchange and anion-exchange moieties.

In an alternative aspect, a polymeric composition of the present invention includes:



25 In one embodiment of this alternative aspect,
m and n are integers greater than zero, p and q are
zero or an integer greater than zero; A₂ and A₃ are
selected from the group consisting of hydrogen,

halogens, alkyls, perfluoroalkyls, $\text{CF}=\text{CF}_2$, CN , NO_2 , OH , $\text{O}-\text{R}$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); B and D are selected from the group consisting of hydrogen, SO_2F , SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 , NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls). In a further embodiment, where m and n are integers greater than zero, at least one of p and q is an integer greater than zero, and the group from which A_2 and A_3 are selected further consists of SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 , NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

In a still further embodiment of a polymeric composition of the above formula, n is an integer greater than zero, and m , p and q are zero or an integer greater than zero; X is SO_2F ; A_2 and A_3 are selected from the group consisting of hydrogen, halogens, alkyls, perfluoroalkyls, $\text{CF}=\text{CF}_2$, CN , NO_2 , OH , $\text{O}-\text{R}$ (where R is selected from the group consisting of alkyls and perfluoroalkyls); X is selected from the group consisting of SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 , NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); B is selected from the group consisting of SO_2F , SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 , NR_3^+

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(where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); D is selected from the group consisting of hydrogen, SO_2F , SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 , NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls). The resulting polymeric compositions may thus comprise homopolymers or copolymers. In a further embodiment, where m and n are integers greater than zero, at least one of p and q is an integer greater than zero, the group from which A_2 and A_3 are selected further consists of SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 , NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

Ion-exchange moieties can be introduced into copolymers containing unsubstituted α,β,β -trifluorostyrene units (so-called "base copolymers") via aromatic substitution of at least a portion of those units. For example, base copolymers incorporating pendant unsubstituted phenyl rings can be sulfonated, phosphorylated, carboxylated, quaternary-aminoalkylated or chloromethylated, and further modified to include $-\text{CH}_2\text{PO}_3\text{H}_2$, $-\text{CH}_2\text{NR}_3^+$ where R is an alkyl, or $-\text{CH}_2\text{NAr}_3^+$ where Ar is a substituted or unsubstituted aromatic group, and other substituents, to provide a cation-exchange or anion-exchange polymeric materials. Further still,

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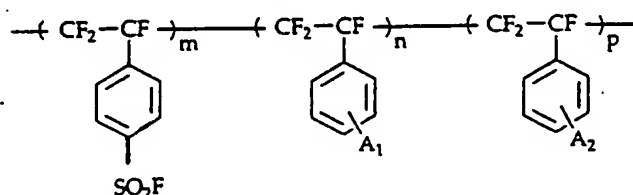
the pendent phenyl moiety may contain a hydroxyl group which can be elaborated by known methods to generate $-\text{OSO}_3\text{H}$, $-\text{OPO}_3\text{H}_2$ and $-\text{OPO}_3\text{H}$ cationic exchange sites on the polymer.

5 In a typical sulfonation reaction used to produce a cationic exchange membrane, the copolymer is dissolved in an appropriate solvent and then reacted with a sulfonating reagent, such as chlorosulfonic acid or a Lewis acid-base complex of
10 sulfur trioxide. The solvent for such a reaction can be selected from the class consisting of chlorinated aliphatic hydrocarbons, such as dichloroethane, tetrachloroethylene and chloroform. The copolymer solution is rendered completely
15 homogeneous prior to the addition of the solution containing the sulfonating reagent. The reaction is then run within the temperature range from about 10°C up to the boiling point of the solvent or preferably in the range of 18°C - 40°C . To ensure
20 adequate functionalization of the copolymer, the reaction is allowed to continue for a period of about one to about four hours, or longer dependent on the reaction temperature.

 Copolymers containing sulfonyl fluoride moiety
25 ($-\text{SO}_2\text{F}$) can be hydrolyzed to generate $-\text{SO}_3\text{H}$ cationic exchange sites on the polymer. In a typical hydrolysis reaction, the sulfonyl fluoride is converted to the free sulfonic acid
 functionality by hydrolysis in concentrated aqueous
30 alkali metal hydroxide at elevated temperatures. This and other procedures for the hydrolysis of $-\text{SO}_2\text{F}$ to $-\text{SO}_3\text{H}$ are well-known to those skilled in the art. The latter approach to the introduction of $-\text{SO}_3\text{H}$ moieties offers advantages over

sulfonation of a base copolymer. For example, it permits greater control over the ion-exchange capacity of the resultant polymer, and hydrolysis is a simpler reaction procedurally than aromatic substitution. In the process typically used for aromatic sulfonation, precipitation of the ionomer prior to reaction of all the available reactive pendant phenyl rings can lead to lower than preferable ion-exchange capacities in the product. Further, this process necessitates an additional purification step prior to membrane preparation. Copolymers containing $-\text{SO}_2\text{F}$ moieties, and no ion-exchange moieties, can be solvent cast or preferably extruded to produce membranes. The resultant membranes can be readily hydrolyzed to give sulfonated membranes as described previously. Extrusion, a method preferable for large-scale membrane production, is further facilitated by the lower glass transition temperatures typical of non-ionomeric copolymers.

Preferred polymeric compositions of the present invention include:



where m , n and p are integers greater than zero and A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3 , and para-phenoxy. These compositions can be converted into compositions incorporating ion-exchange moieties using techniques elaborated above.

As used herein, the term "aryl" refers to a substituted or unsubstituted aromatic group.

The substituents on the aromatic rings (SO_2F , A_1 , A_2 , A_3 , X , B and D) in the embodiments described
5 above may be located in the ortho, meta or para positions. In preferred aspects of the described embodiments, the substituents are in the meta or para positions.

The copolymers thus prepared possess favorable
10 properties, such as thermal stability, chemical resistance and favorable mechanical properties, such as tensile strength, compared to the homopolymeric material formed from α,β,β -tri-fluorostyrene (TFS) alone.

15 Crosslinking can be introduced using conventional techniques well-known to those skilled in the art, such as those employed in preparing divinylbenzene crosslinked polystyrene. Crosslinking, for example to enhance the mechanical
20 and physical properties of the membrane material, can be introduced by reaction of appropriate groups, before or preferably after the claimed polymeric compositions are formed into membranes. Monomers with substituents on the pendant phenyl
25 rings which are suitable for subsequent crosslinking can be introduced into the copolymer in controlled amounts, thereby permitting some control of the degree of crosslinking in the membrane.

30 The following examples are for purposes of illustration and are not intended to limit the invention. Example 1 describes the synthesis of the monomer, p-sulfonyl fluoride α,α,β -trifluorostyrene from iodobenzene. Example 2

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describes the emulsion copolymerization of p-sulfonyl fluoride- α,β,β -trifluorostyrene, α,β,β -trifluorostyrene and m-trifluoromethyl- α,β,β -trifluorostyrene. Example 3 describes the emulsion
5 copolymerization of p-phenoxy- α,β,β -trifluorostyrene, α,β,β -trifluorostyrene and m-trifluoromethyl- α,β,β -trifluorostyrene. Examples 4 and 5 describe generalized procedures which may be used to prepare the claimed polymeric
10 compositions. Example 4 describes a typical emulsion polymerization reaction which can be used for one or more monomers (solid or liquid) to make a homopolymer or copolymer, respectively. Example 5 describes a typical hydrolysis procedure which
15 may be used to convert $-\text{SO}_2\text{F}$ moieties to $-\text{SO}_3\text{H}$.

Example 1

p-Sulfonyl fluoride- α,β,β -trifluorostyrene

(a) p-Iodobenzenesulfonyl chloride is prepared according to the method described in P.
20 Sanecchi, Polish Journal of Chemistry, Vol.66, 101-110 (1992):

To a dry 5 L three-neck round-bottom flask fitted with mechanical stirring, heating mantle, water-cooled condenser with adapter hose connected
25 to an HCl trap, 2 L addition funnel and inert gas inlet is added 2.5 L of chloroform and chlorosulfonic acid (503 g, 4.32 mol). The mixture is heated to a gentle reflux and a solution of iodobenzene (400 g; 1.96 mol) in 0.5 L of
30 chloroform is added over a period of 1 hour, during which time the reaction mixture changes color from yellow to dark red-purple, with evolution of HCl.

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The reaction is heated for a further 1 hour at reflux. Analysis by GC indicates complete conversion to p-iodobenzenesulfonyl chloride. The reaction is worked-up by pouring the mixture into a 6 L separatory funnel, and discarding the lower, mostly mineral acid, layer. The organic layer is neutralized and dried over MgSO_4 . Solvent evaporation affords p-iodobenzenesulfonyl chloride as a crude yellow solid; yield approximately 593 g (quantitative). The product may be further purified by distillation under high vacuum, if desired.

(b) p-Iodobenzenesulfonyl fluoride is prepared using a method similar to that described in U.S. Patent No. 3,560,568 issued February 2, 1971:

p-Iodobenzenesulfonyl chloride (593 g, 1.96 mol), prepared as described in Example 1(a) above, is dissolved in 2.5 L of acetone and placed in a 5 L three-neck round-bottom flask fitted with a heating mantle, mechanical stirring and a water-cooled condenser. Potassium fluoride (126 g, 2.17 mol) and about 25 mL of water is added and the reaction is heated at reflux for approximately 5 hours. On cooling, the reaction mass is filtered and the solvent removed to provide a crude solid, which on purification, by distillation under high vacuum, affords p-iodobenzenesulfonyl fluoride as a white solid; yield 504 g (90%).

(c) 1,1,2-Trifluoroethenyl zinc bromide bromotrifluoroethylene (106g, 0.66 mol) in DMF, prepared according to the method described in P.L. Heinze and D.J. Burton, Journal of Organic Chemistry, Vol. 53, 2714-2720 (1988), is added to a

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1 L, three-neck round-bottom flask fitted with water-cooled condenser and inert gas inlet. p-Iodobenzenesulfonyl fluoride (128.5 g, 0.45 mol) prepared as described in Example 1(ii),

5 palladium(0) bis(dibenzylidene acetone) (1.60 g, 2.8 mmol) and triphenylphosphine (1.86 g, 7.1 mmol) were added and the reaction is heated slowly to about 55°C at which point the heat generated by the reaction is used to maintain the temperature at no

10 higher than about 100°C (cooling provided by an ice water bath). When the exotherm has subsided, the cooling bath is removed and external heating used to maintain the reaction at 75°C for 3 hours. The reaction is then flash distilled under high vacuum

15 (<1 mm Hg), isolating greater than 90% of the liquid components. The distillate is poured into a 2 L separatory funnel containing 1 L of deionized water. The products in the separatory funnel were then extracted with pentane (3 x 250 mL). The

20 pentane extracts were combined, washed with water (3 x 250 mL), dried over anhydrous MgSO₄, filtered and evaporated to leave a clear yellow viscous liquid. The crude product is distilled under high vacuum to yield the title compound, p-sulfonyl

25 fluoride- α,β,β -trifluorostyrene, (74.8 g, 69%) as a clear, pale yellow liquid. Infrared data in accord.

Example 2

Emulsion copolymerization of p-sulfonyl fluoride-

30 α,β,β -trifluorostyrene, m-trifluoromethyl-
 α,β,β -trifluorostyrene and α,β,β -trifluorostyrene

To a 1 L three-neck flask, fitted with a

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water-cooled condenser, inert gas inlet and thermocouple, is added 350 mL of nitrogen-degassed water, dodecylamine hydrochloride (6.80 g, 27 mmol) and the following monomers: α,β,β -trifluorostyrene (13.3 g, 85 mmol), m-trifluoromethyl- α,β,β -trifluorostyrene (9.90 g, 85 mmol) and p-sulfonyl fluoride- α,β,β -trifluorostyrene (40 g, 0.167 mole). The initiator, potassium persulfate (0.52 g, 1.8 mmol) is added and the reaction temperature elevated to 50°C and held at this temperature for approximately 72 hours. Initial work-up of the reaction affords a yellow powder; yield 63.1 g (quantitative), intrinsic viscosity $[\eta] = 1.79$ dL/g as determined in toluene at 30°C. ^{19}F -NMR analysis performed on a VARIAN XL-300 NMR instrument using CDCl_3 as solvent is used to confirm incorporation of all three monomer fragments.

Example 3

Emulsion copolymerization of p-phenoxy- α,β,β -trifluorostyrene, α,β,β -trifluorostyrene and m-trifluoromethyl- α,β,β -trifluorostyrene

To a 500 mL three-neck flask, fitted with a water-cooled condenser, inert gas inlet and thermocouple, is added 350 mL of nitrogen-degassed water, dodecylamine hydrochloride (4.57 g, 21 mmol) and the following monomers: α,β,β -trifluorostyrene (4.57 g, 30 mmol), m-trifluoromethyl- α,β,β -trifluorostyrene (6.76 g, 30 mmol), p-phenoxy- α,β,β -trifluorostyrene (22.44 g, 90 mmol). The initiator, potassium persulfate (0.39 g, 1.4 mmol) is then added and the reaction temperature elevated to 50°C and held at this temperature for

approximately 72 hours. Work-up of the reaction affords a pale yellow powder; yield 25.5 g (75%).

Example 4

General Emulsion Copolymerization Procedure

5 To a 12 L reaction vessel equipped with a stirrer, water-cooled condenser, heating mantle and temperature controller is added 3.2 L of water. The water is degassed with nitrogen for approximately one hour and the reaction is kept
10 under a nitrogen atmosphere throughout. Dodecylamine hydrochloride (58 g, 0.26 mol) is added and stirred into the water. At this point the desired monomers (which may be pre-mixed) are added to the vessel with stirring, to form an
15 emulsion. The temperature of the emulsion is increased to 50°C and potassium persulfate (4.42 g 15 mmol) is added. The reaction is allowed to continue for approximately 72 hours. Subsequently, 2 L of water is added to dilute the emulsion,
20 followed by a solution of potassium hydroxide (80 g, 1.43 mol) dissolved in 2 L of water. The precipitated polymer is then stirred vigorously for up to one hour at 75°C. The mixture upon cooling is filtered, the filter cake being washed several
25 times with fresh water. Having removed the majority of the filtrate, the cake is then transferred into a Soxhlet thimble and washed by continuous extraction with refluxing methanol to give a random, linear copolymer of the monomers
30 introduced. The resultant product (typically an off-white powder) is sufficiently pure for further elaboration.

Example 5**General Hydrolysis Procedure**

5 The polymer, preferably in the form of a membrane, is treated with an excess of 6N aqueous potassium hydroxide at 80°C for approximately 18 hours. The polymer is then washed with deionized water to remove unreacted potassium hydroxide and potassium fluoride by-product.

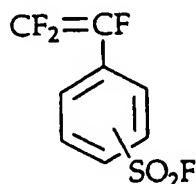
10 Copolymers prepared from monomer mixtures including sulfonyl fluoride- α,β,β -trifluorostyrene are produced in yields greater than 80%, and are converted essentially quantitatively to the corresponding sulfonic acid analogues by hydrolysis.

15 While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in
20 the art, particularly in light of the foregoing teachings. It is therefore contemplated by the appended claims to cover such modifications as incorporate those features which come within the spirit and scope of the invention.

What is claimed is:

1. A compound having the chemical formula:

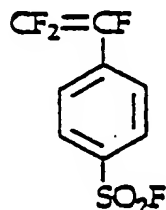
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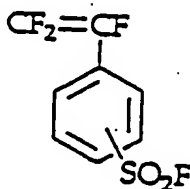
2. A compound having the chemical formula:

15



3. A homopolymer of:

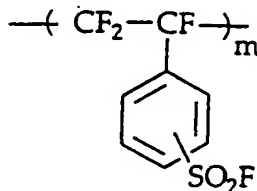
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4. A polymeric composition comprising:

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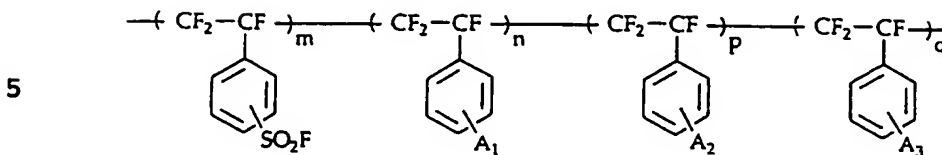


where m is an integer greater than zero.

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- 21 -

5. A polymeric composition comprising:



10 where m is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; and A₁, A₂ and A₃ are selected from the group consisting of hydrogen, halogens, alkyls, perfluoroalkyls, CF=CF₂, CN, NO₂, OH, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

15

6. The polymeric composition of claim 5 wherein the group from which A₁, A₂ and A₃ are selected further consists of SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, OPO₃H₂, NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), and at least one of A₁, A₂ and A₃ is selected from the group consisting of SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, OPO₃H₂, NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

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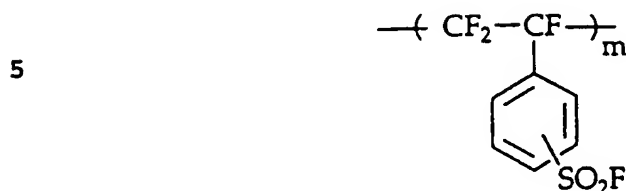
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7. A polymeric composition according to any of claims 3-6 wherein the composition is at least partially crosslinked.

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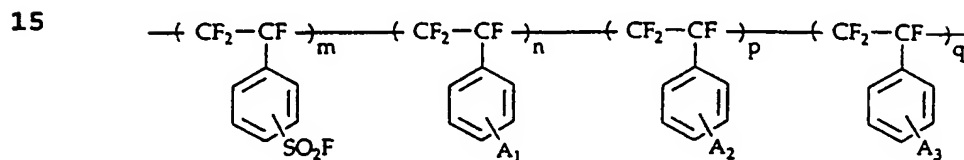
- 22 -

8. A polymeric composition consisting essentially of:



10 where m is an integer greater than zero.

9. A polymeric composition consisting essentially of:



20

where m is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A₁, A₂ and A₃ are selected from the group consisting of hydrogen, halogens, alkyls, perfluoroalkyls, CF=CF₂, CN, NO₂, OH, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

25

10. The polymeric composition of claim 9 wherein the group from which A₁, A₂ and A₃ are selected further consists of SO₃H, PO₃H₂, PO₃H, CH₂PO₃H₂, COOH, OSO₃H, OPO₃H₂, OPO₃H, NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group consisting of alkyls,

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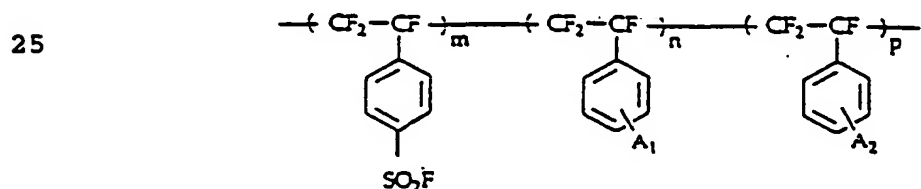
perfluoroalkyls and aryls), and at least one of A_1 , A_2 and A_3 is selected from the group consisting of SO_3H , PO_2H_2 , PO_3H_2 , $CH_2PO_3H_2$, $COOH$, OSO_3H , OPO_2H_2 , OPO_3H_2 , NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

11. A polymeric composition according to any of claims 8-10 wherein the composition is at least partially crosslinked.

12. A polymeric membrane comprising a polymeric composition according to any of claims 3-11.

13. A polymeric membrane consisting essentially of a polymeric composition according to any of claims 3-11.

14. A polymeric composition comprising:

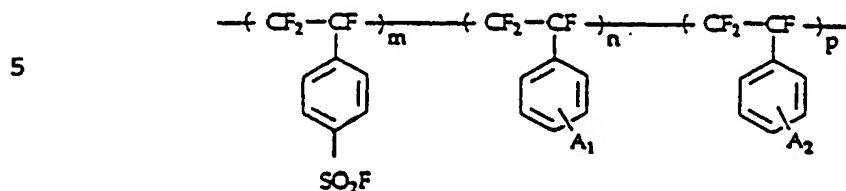


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where m, n and p are integers greater than zero and A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3 and para-phenoxy.

35

15. A polymeric composition consisting essentially of:



10 where m, n and p are integers greater than zero and A₁ and A₂ are selected from the group consisting of hydrogen, fluorine, CF₃ and para-phenoxy.

15 16. An ion exchange membrane comprising a polymeric composition according to either of claims 6 and 10.

20 17. An ion exchange membrane consisting essentially of a polymeric composition according to either of claims 6 and 10.

25 18. An electrochemical fuel cell comprising the ion exchange membrane of claim 16.

30 19. An electrochemical fuel cell comprising the ion exchange membrane of claim 17.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA 96/00370

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C07C 309/86, C08L 27/00, C08F 212/14, H01M 8/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C07C, C08F, H01M, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STN International, File CAPLUS, CAPLUS accession no. 1974:551737, M.V. Stepanov et al: "Synthesis of sodium salts of halo derivatives of p-vinylbenzenesulfonic acids", Zh. Org. Khim. (1974), 10(9), 1927-31 --	1-2
X	STN International, File CAPLUS, CAPLUS accession no. 1976:135746, L.F. Rybakova et al: "Synthesis and properties of trimethylsilyl esters of fluoro-containing vinylbenzenesulfonic acids", Zh. Obshch. Khim. (1976), 46(1), 117-21 --	1-2
A	DE, B, 1127340 (FARBWERKE HOECHST AKTIENGESELLSCHAFT), 12 April 1962 (12.04.62), column 5, line 17 - line 35, the claim --	1-2

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

<ul style="list-style-type: none"> * Special categories of cited documents "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed 	<ul style="list-style-type: none"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
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Date of the actual completion of the international search

2 Sept 1996

Date of mailing of the international search report

25.09.96

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA 96/00370

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4012303 (V.F. D'AGOSTINO ET AL), 15 March 1977 (15.03.77) --	1-19
A	US, A, 3341366 (R.B. HODGDON, JR. ET AL), 12 Sept 1967 (12.09.67) -- -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

31/07/96

International application No.

PCT/CA 96/00370

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-B- 1127340	12/04/62	NONE	
US-A- 4012303	15/03/77	BE-A- 836970	22/06/76
		DE-A- 2558393	24/06/76
		FR-A- 2295982	23/07/76
		GB-A- 1498990	25/01/78
		JP-A- 51089881	06/08/76
		NL-A- 7514956	25/06/76
		SE-A- 7514517	24/06/76
		US-A- 4107005	15/08/78
		US-A- 4113922	12/09/78
US-A- 3341366	12/09/67	BE-A- 668486	16/12/65
		CH-A- 463462	00/00/00
		DE-A,B,C 1570681	12/03/70
		FR-A- 1452148	00/00/00
		GB-A- 1096879	00/00/00
		NL-A- 6510859	21/02/66
		SE-B- 337921	23/08/71
		US-A- 3442825	06/05/69